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A STUDY OF THE THEORIES REGARDING SOIL ACIDITY

By

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A STUDY OF THE THEORIES REGARDING SOIL ACIDITY

INTRODUCTION

The problem of soil acidity has been one of the most important with which the science of agriculture has had to deal. It has been known for years that a great many of the soils of this country are acid and that acid soils are becoming more prevalent. Accordingly the attention of a great many experimentors has been directed towards an investigation of this problem.

Since the problem is very complex a great many theories as to the nature and causes of soil acidity have been brought forth. These theories have been modified until the present time when there remain only two theories, the true acid theory and the selective ion adsorption theory. It is not necessary that these two theories be discussed at any great length in this paper, nor is it desirable that a complete review of the work on these two theories be made here. It is necessary, however, that the fundamental facts and arguments concerning the two theories be stated. Therefore a brief review follows.

The True Acid Theory

The supporters of this theory believe that the acid reaction of acid soils is due to true acids in the soil, principally acid silicates in mineral soils, and that when an acid soil is treated with a neutral salt solution the soluble acid liberated is due to double decomposition.

One of the causes that gave rise to the adsorption theory of soil acidity was Cameron's(2) experiment with adsorbent cotton and litmus from which he concluded that the cotton adsorbed the basic ion of the litmus. Truog(7) has since shown conclusively that Cameron's explanation is erroneous since the phenomenon is due to a true chemical reaction between the water insoluble acids of the cotton and the base of the litmus.

Truog(7) has also shown that when side reactions are eliminated approximately equivalent amounts of bases are retained when an acid soil is treated with salt solutions having the same acid radical. This is in accordance with the law of affinity of acids.

Data upon this subject also show that the stronger the acids of salts having the same base the less the amount of base retained by the soil. This is also in accord with the law of affinity of acids.

Armsby(1) pointed out that the equilibria relations which obtain when soils are treated with salt solutions could be clearly explained on the basis of the law of mass action.

Robertson(6) also showed that there is a close relationship between adsorption and mass action.

Rice(5) observed that in the reaction which takes place with soils and salt solutions equivalent amounts of bases are given up for those retained.

Wolkoff(9) concluded that for the soils studied the reaction between the salts and soil colloids was in accordance with the law of mass action.

The Selective Ion Adsorption Theory

This theory is based on the assumption that the colloidal matter of the soil has the power of adsorbing the cation of a neutral salt solution thereby liberating a free acid.

The advocates of this theory divide all acid soils into two groups: those soils that are truly acid and give an aqueous extract which is acid toward litmus; and those soils that do not give an aqueous extract which is acid toward litmus but do give an acid extract when treated with neutral salt solutions. In the case of the latter soils they hold that the acid extract is not due to double decomposition between the insoluble acids of the soils and the salt solution but that it is due to the adsorption of the basic ion of the salt with the liberation of a soluble acid.

The principal observations made in support of this theory are here stated.

Cameron(3), from his experiments with adsorbent cotton and litmus, concluded that soils like cotton exert a selective adsorption for the basic ion of the litmus.

Harris(4) reached the following conclusions:

1. That equivalent amounts of bases from salt solutions having the same acid radical are not retained by the soil but that the amount of cations adsorbed follows the valence rule for the precipitation of colloids.

2. That the formation of a soluble acid by the double decomposition of the insoluble acids of the soil and the salt

solution is contrary to the law of mass action unless the new salt formed is more insoluble than the original acid and that this was highly improbable in the soil reaction.

3. That the amount of cations retained by the soil from a salt solution follows the adsorption equation, namely $\frac{x}{m} = AC^{\frac{1}{n}}$.

Wiegner(8) observed that the exchange of bases between soil silicates and neutral salts conforms closely with the adsorption formula.

EXPERIMENTAL

Purpose of the Experiments

The object of the experiments described in this paper was threefold: first, to see if a true insoluble acid would be analogous to acid soils in its reaction toward litmus and salt solutions; second, to see if the factors affecting adsorption apply in the soil reaction; and third, to find out if there is a close relationship between mass action and adsorption.

Apparatus and Materials Used

It was realized from the initial experiments that since temperature and rate of stirring of the solutions are important factors, they should be controlled. Accordingly a thermostat regulated to .02° C and equipped with a stirring device by which all the solutions could be stirred at a constant rate was set up.

All chemicals used were (Merck's) chemically pure. Salt solutions were made up with carbon dioxide free water on the basis of half normality except where otherwise stated. These solutions were made neutral to phenolphthalein.

The soils used were Marshall silt loam and Superior clay. The former contained a high percentage of organic matter, the latter contained a small amount. Both of these soils were typical acid soils in their reactions. Each gave a water extract that was neutral to litmus but reacted when in contact, and gave an acid extract when treated with a salt solution. Each soil was well mixed, pulverized, and put through a forty mesh sieve.

Procedure

In the experiments with soils twenty-five gram samples of soil were treated with 125 c.c. of salt solution. These were well mixed in an Erlenmeyer flask and then placed in the thermostat which had been regulated to the desired temperature. The mixture was kept in a constant state of agitation by means of stirring rod. After the reaction had gone the desired length of time the mixture was filtered on a Büchner funnel and a 100 c.c. aliquot taken for titration with N/25 NaOH which was free from carbonates.

In the experiments with stearic acid a one gram sample of stearic acid was used. The remainder of the procedure was the same as where soil was used except where otherwise stated.

Experiment 1

The object of this experiment was to see if an insoluble acid is analogous to an acid soil in its reaction, and to see if the factors affecting adsorption apply in the soil reaction.

In order to see if an insoluble acid is analogous to an acid soil in its reactions with salt solutions, stearic acid was treated with a half normal solution of potassium acetate. The reasons for selecting stearic acid were that it could be obtained in a high state of purity, was a very insoluble acid and reacted toward litmus when in contact but gave an aqueous solution that was neutral.

Gibbs(3) has shown that in a two phase system consisting of a liquid and a solid any substance which will reduce the sur-

face tension of the liquid will be adsorbed. Consequently if soil acidity is due to adsorption an increase in temperature should decrease the amount of adsorption, since surface tension decreases with a rise in temperature. Michaelis(3) has shown that adsorption varies with the surface tension of the solvent and that the variation is in the same direction. Since alcohol has a surface tension of only a fraction of that of water it follows that there should be less adsorption from an alcoholic solution than from an aqueous one.

In order to see if these two factors had this effect in the soil reaction samples of soil were treated with aqueous and alcoholic solutions of potassium acetate at different temperatures.

It will be noted from data of Table 1 that the insoluble stearic acid reacts in every respect like the insoluble acids of the soil. It liberates a soluble acid from a salt solution and, like the soil, the greater the temperature at which the reaction takes place, the greater is the velocity of the reaction and the greater the amount of acid liberated.

To show conclusively that when stearic acid is treated with potassium acetate solution the acidity of the extract is due to acetic acid liberated by the reaction of the salt with the insoluble stearic acid and not to stearic acid that has simply gone into solution the following experiment was performed: A sample of stearic acid was treated with potassium acetate solution, filtered, and the acid of the extract titrated with

Table 1

The effect of temperature, time and solvent an soluble acid liberated when soils and stearic acid are treated with potassium acetate solutions indicated. Figures give c.c. of N/25 acid liberated.

Solutions used

Time of Contact	N/2 aqueous solution of potassium acetate								N/2 alcoholic solution of potassium acetate (95% alcohol)	
	Stearic Acid at Temperature of		Superior Clay at Temperature of			Marshall silt loam at Temperature of			Superior Clay at Temp. of 28°	Marshall silt loam at Temp. of 28°
	28° C	40° C	28° C	40° C	50° C	24° C	40° C	50° C		
10 min.	2.6	20.2	13.9	14.9	16.3	20.4	23.9	26.5		
30 min.	3.6	21.5	14.5	15.6	17.1	20.68	25.2	27.1		
1 hr.	4.9	22.7	14.6	16.35	17.7	21.2	25.5	28.4		
2 hrs.				16.55	18.4	21.9		29.6		
3 hrs.									32.5	47.5
4 hrs.	7.1	24.4	15.0	17.00	18.9		26.5	30.35		
6 hrs.	7.7	25.0		18.00	18.8	22.9	27.2	31.1		
18 hrs.	10.0	25.45	15.8	12.00	14.5	22.5	27.1	34.5	35.5	52.8
24 hrs.	11.0	26.00	16.0	11.00	9.6	22.7	27.7	34.3		

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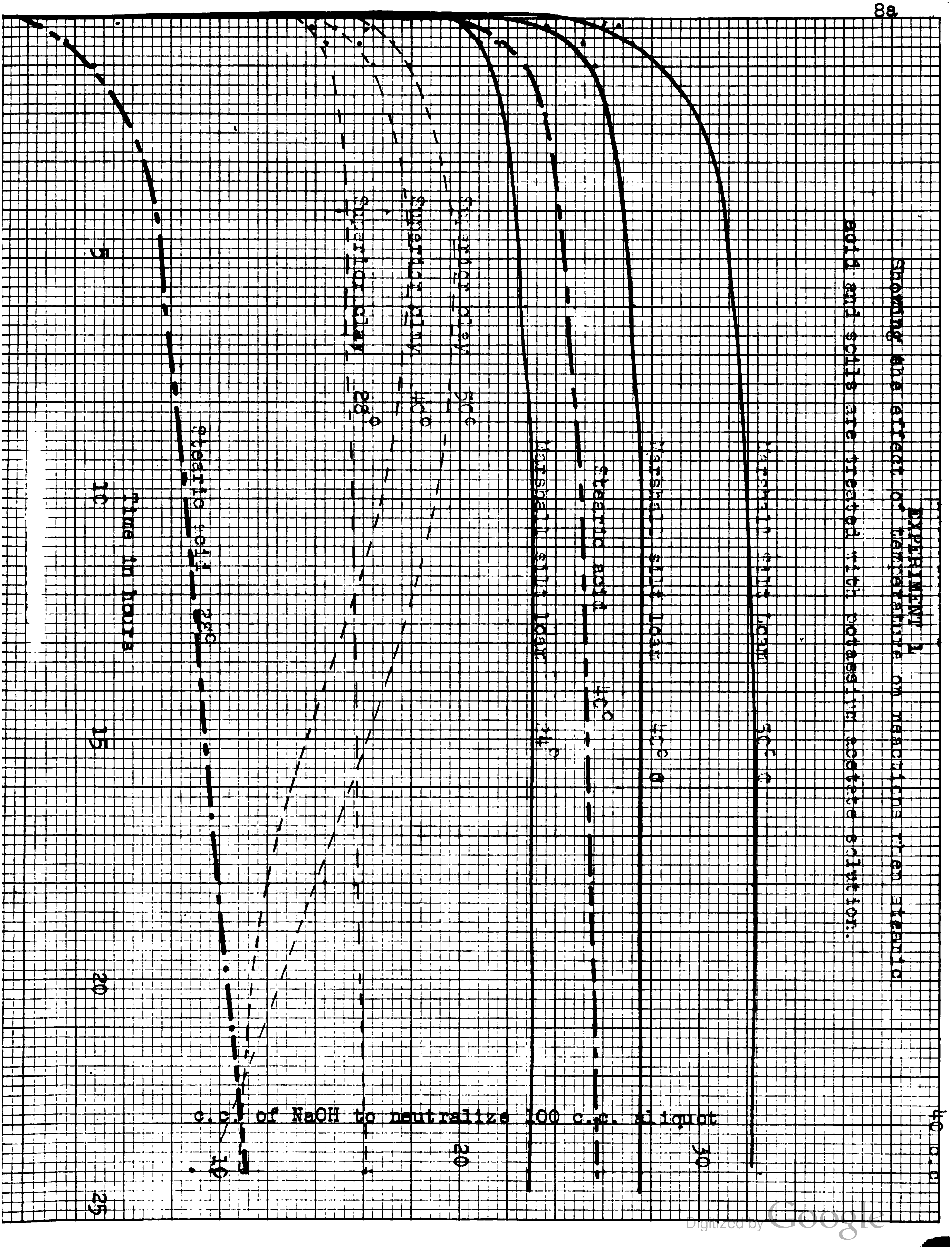

EXPERIMENT 1
Showing the effect of temperature on reactions when stearic acid and soils are treated with potassium acetate solution.
Stearic acid 22c
Superior clay 28c
Superior clay 40c
Superior clay 50c
Marshall silt loam 24c
Stearic acid 40c
Marshall silt loam 40c
Marshall silt loam 50c
Time in hours
5
10
15
20
25
c.c. of NaOH to neutralize 100 c.c. aliquot
10
20
30
40 c.c.

N/25 sodium hydroxide. The extract required 18.3 c.c. N/25 sodium hydroxide to neutralize the acidity. The stearic acid was then washed and treated with 125 c.c. of N/25 hydrochloric acid and again filtered. The resulting extract required 107.2 c.c. of N/25 sodium hydroxide to neutralize the hydrochloric acid, leaving a difference of 17.8 c.c. of N/25 hydrochloric acid which had been neutralized by a stearate. It is evident, therefore, that the difference between the amount of hydrochloric acid used and the amount of sodium hydroxide necessary to neutralize the hydrochloric acid extract was closely equivalent to the amount of acid liberated when the stearic acid was treated with potassium acetate solution. The explanation of this equivalence is that the stearic acid reacted with the potassium acetate to form potassium stearate. The latter salt when treated with hydrochloric acid reacted with the acid to form a neutral salt and an insoluble acid, thus neutralizing a part of the hydrochloric acid.

It is also to be noted from Table 1 that for both soils the higher the temperature at which the reaction took place the greater was the maximum amount of acid liberated. This is contrary to adsorption phenomena but is in accordance with chemical dynamics. In the case of the alcoholic solutions the total acidity liberated was far greater than in the case of the aqueous solutions, a fact which again is contrary to adsorption.

Experiment 2, Adsorption and Mass Action

Since Armsby and Robertson had pointed out that there is a close relationship in certain respects between adsorption and mass action it seemed desirable to discover if a close analogy, mathematically and experimentally, could be drawn between the two.

The adsorption isotherm equation that has been used for soils is $\frac{x}{m} = AC^{\frac{1}{n}}$ where

x = amount of basic ion adsorbed

m = amount of adsorbing medium (soil)

A = constant depending upon character of two phases

C = end concentration of substance adsorbed

$\frac{1}{n}$ = constant depending upon the two phases

In this equation, as applied to soils, m, the amount of soil used, has been kept a constant so that the equation can be simplified, thus:

$$x = mAC^{\frac{1}{n}}$$

$$mA = \text{constant}$$

$x = AC^{\frac{1}{n}}$ in which A now has a different value

or

$$x^n = A^nC$$

$$\frac{C}{x^n} = \frac{1}{A^n} = \text{constant} = K$$

$$\frac{C}{x^n} = K$$

C = end concentration or $(a-x)$ where a = initial concentration,

therefore

$$\frac{a - x}{x^n} = K$$

One of the general equations for mass action is

$$\frac{(a-x)\ (b-x)}{x^2} = K$$

Where a and b are initial concentrations of two reacting substances

x = amount reacted

K = constant depending upon the reacting substances.

If this equation be applied to the soil reaction with salt solutions and b be taken to equal initial concentration of insoluble acids in the soil, then (b-x) may be considered to be practically a constant in so far as it affects the derivation of $\frac{1}{n}$. For while (b-x) may vary 25 to 50 per cent, yet this variation has such little effect upon the exponent of the denominator that when the exponent is to be derived (b-x) may be considered a constant without any appreciable variation in the actual value of the exponent.

The mass law equation, therefore, as applied to soils in this case may be written

$$\frac{a-x}{x^2} = \frac{K}{b-x} = \text{constant}$$

or

$\frac{a-x}{x^2} = K$ in which K now has a different value.

The adsorption equation $\frac{a-x}{x^n} = K$, therefore, differs from the mass law equation only in the exponent of the denominator. It will be remembered, however, that the value for n in the ad-

sorption equation varies from two to ten and for soil reactions is generally about two. We would, therefore, expect that certain kinds of mass law data could be substituted in the adsorption equation with the derivation of the constant $\frac{1}{n}$.

In order to see if such is the case the following experiment was performed:

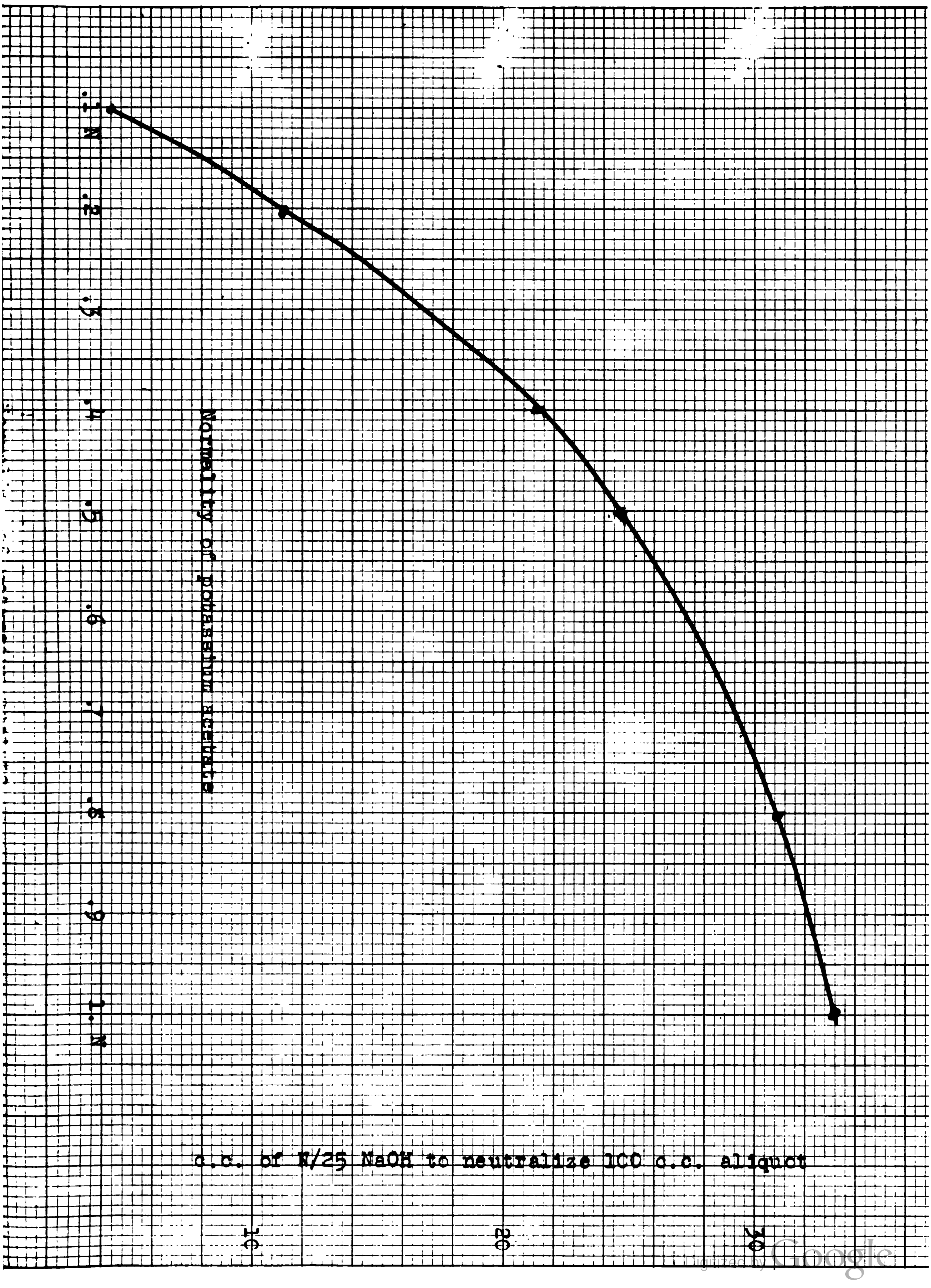
A one gram sample of stearic acid was treated with 125 c.c. of potassium acetate solution of varying normality at 40° C and constantly stirred for one hour. The solution was then filtered on a Büchner funnel and 100 c.c. titrated with N/25 sodium hydroxide. From the data thus obtained the initial concentration of salt present, the end concentration, and the amount that had reacted were calculated and substituted in the formula $\frac{C}{x^n} = K$ and the constant $\frac{1}{n}$ calculated as given in Table 2.

This experiment clearly shows that mass law data, or data derived from purely chemical reactions, may be substituted in the adsorption equation with the derivation of the constant $\frac{1}{n}$. The values thus obtained compare favorably for their constancy with those values which have been obtained when soils are used and which have been offered as proof that the phenomenon is one of adsorption.

Table 2

Soluble acid liberated by treatment of stearic acid with potassium acetate solutions of strengths indicated, and substitution of data in the adsorption equation with the derivation of the constant $\frac{1}{n}$.

Normality of potassium acetate used	Gms. of potassium acetate in 100 c.c. aliquot	Acid liberated in c.c. of N/25 NaOH	Gms. of potassium acetate reacted	Conc. of potassium acetate after reaction	Value for $\frac{1}{n}$	Value for K
1. N	9.80	33.3	.131	9.679	.893	94.29
.8 N	7.84	31.1	.122	7.618	.840	94.29
.5 N	5.88	24.8	.0972	5.783	.840	94.29
.4 N	3.92	21.1	.0827	3.8373	.80	94.29
.2 N	1.96	11.15	.0435	1.9165	.80	94.29
.1 N	.98	4.25	.01666	.9633	.893	94.29


Normality of potassium acetate
.1 N
.2
.3
.4
.5
.6
.7
.8
.9
1.0 N
c.c. of N/25 NaOH to neutralize 1CO c.c. aliquot
10
20
30

DISCUSSION

Experiments described in this paper with stearic acid and potassium acetate show the fallacy of the argument that the liberation of a soluble acid from an insoluble one is contrary to the law of mass action. These experiments also show that the reaction of an insoluble acid is in all respects analogous to the reaction of acid soils.

It can be seen from the experiment with soil solutions at different temperatures and with solvents of different surface tensions that the data are not in accordance with adsorption phenomena. The effect of these two factors is the converse of what it would be if the reaction was one of adsorption, but is in accordance with true chemical reactions.

Since the experiments described in this paper show that the adsorption equation and the mass action equation as applied to soils are closely related it would naturally be expected that the soil reaction with salt solutions would conform with the adsorption equation. It is to be noted in this respect, however, that in all the data in which this method of proof of adsorption is offered the constant $\frac{1}{n}$ is derived instead of the constant A (or K). The constant $\frac{1}{n}$ is an exponent and as such it would not be expected to vary considerably. In all the data upon this equation as applied to soils the constant $\frac{1}{n}$ as derived does not vary appreciably yet the variation is sufficient to cause the other constant A in the equation to vary considerably. Another fallacy in this method of proof of adsorption as sometimes given

is the fact that the initial concentration of the basic ion is used whereas the equation calls for the end concentration. This error makes the proof of no value.

In conclusion as regards the value of this argument it is sufficient to quote Zsigmondy(10) upon this equation. "It should not be overlooked that the adsorption isotherms already given are typical for true adsorption phenomena; and wherever these isotherms fit the case many experimenters regard the reactions as pure adsorption even when there is some evidence to the contrary. It should also be remembered that the formula has no theoretical foundation, and that the incorporation of two constants makes it a very flexible interpolation formula."

SUMMARY

All data upon this subject go to show that the reaction between acid soils and salt solutions is in accordance with true chemical reactions and not with adsorption.

Experiments described in this paper show:

That in all respects the reaction of an acid soil with potassium acetate is analogous to the reaction of an insoluble acid.

That the formation of soluble acids by the action of soluble neutral salts on insoluble acids is not contrary to the law of mass action.

That the factors of temperature and solvent which influence the reaction between acid soils and neutral salt solutions have an opposite effect to what they would have if the reaction was one of adsorption.

That the derivation of the constant $\frac{1}{n}$ in the adsorption equation is not a proof of adsorption since mass action data obtained from chemical reactions between solutions and insoluble substances can be substituted in the adsorption equation with the derivation of the constant $\frac{1}{n}$ with just as satisfactory results as when true adsorption data are used.

REFERENCES

1. Armsby, H. P., Landw. Vers. Sta., 21, 397 (1878).

2. Cameron, F. K., U. S. Dept. Agr., Bur. Soils Bull. 30, 60 (1905) also "The Soil Solution".

3. Gibbs, W., Scientific Papers (London 1906), Vol. 1. See also Michaelis, The Dynamics of Surfaces, page 5, (1914).

4. Harris, J. E., Jour. Phys. Chem. 6, 21 (1917).

5. Rice, F. E., Jour. Ag. Res. 1, 179 (1913).

6. Robertson, Jour. Biol. Chem., 4, 38 (1908).

7. Truog, E., Jour. Phys. Chem., Vol. 20, No. 6 (1916).

8. Wiegner, Jour. of Landw., 60, 111 (1912).

9. Wolkoff, M. I., Soil Science, Vol. 1, 6 (1916).

10. Zsigmondy, R., Chemistry of Colloids, page 62 (1917).

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